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The Stability of Evaporated Fe Films Sandwiched with Various Materials; A Mössbauer Study

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Multilayer Fe films sandwiched with Rh, B, Sn, Sb, and MgF_2 were prepared by the alternate deposition in UHV deposition system. The compounds formed at the interface layer of Fe film coated with some materials were determined by the Mössbauer spectroscopy. Some compounds were found at the interface between Fe films and coating Rh or B. In the Fe-Sn multilayer film, all of Fe atoms are in the state of some intermetallic compounds like FeSn and FeSn_2 . The Sb-coated Fe films as-deposited are stable up to 370K, but all of Fe atoms transformed to FeSb_2 at 490K. Fe films coated by MgF_2 are also stable, but the grain growth of Fe film occurs after the thermal treatment at 480K in vacuum for twenty days. In this paper, the mechanism of the compound formation at the interface layer is also discussed.

KEY WORDS Mössbauer effect/ Thin film/ Magnetism/

INTRODUCTION

Vacuum deposited thin Fe films are suitable for the study of surface magnetic properties by means of Mössbauer spectroscopy. In UHV atmosphere, Fe and various coating materials were alternately evaporated. We have succeeded in preparing Fe films of various thicknesses sandwiched with MgF_2 , MgO , and Sb layers and measured the Mössbauer spectra. The thickness dependence of the magnetic properties was studied and the interface magnetism was discussed.^{1,2,3)}

In general, very thin films are chemically less stable and vapor deposited atoms have high reactivity. Deposited atoms do not always form a uniform thin film on the substrate but easily diffuse into the substrate and form some compounds. Even in UHV atmosphere, various kinds of contaminations are very probable. Products by vacuum depositions depend on the temperature of the substrate, deposition rate, chemical reactivity between the substrate and the deposited atoms, impurities and so on. This note reports some Mössbauer results concerning the stability of vacuum deposited Fe films. Mössbauer spectra show the situation of Fe atoms at the interfaces very clearly. Therefore Mössbauer measurements are very useful for the characterization of thin films.

SAMPLE PREPARATION

Coating material and Fe were alternately deposited in an ultra high vacuum deposi-

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Stability of Evaporated Fe Films

Table I. The Multilayer Samples for Mössbauer Measurements

| sample | the order of evaporation process | repetition* |
|------------|---|-------------|
| FRH-1 | [Rh(150Å) - Fe(24Å)] - Rh(240Å) | three times |
| FRH-4 | Rh(240Å) - [Fe(16Å) - Rh(160Å)] - Fe(16Å) - Rh(200Å) | three times |
| FRH-6 | Rh(160Å) - [Fe(8Å) - Rh(120Å)] | eight times |
| FB-1 | B(400Å) - [Fe(16Å) - B(320Å)] - Fe(16Å) - B(520Å) | twice |
| FB-2 | B(400Å) - Fe(32Å) - B(720Å) | |
| FB-3 | B(360Å) - Fe(24Å) - B(240Å) - Fe(24Å) - B(520Å) | |
| FSN-1 | Sn(400Å) - Fe(48Å) - Sn(640Å) | |
| "Sn on Fe" | Fe(48Å) - Sn(480Å) | |
| "Fe on Sn" | Sn(480Å) - Fe(48Å) | |
| FSB-12 | [Sb(240Å) - Fe ⁵⁶ (120Å) - Fe ⁵⁷ (4Å)] - Sb(320Å) | ten times |

* the repeating times for the process in the brackets.

tion system onto a mylar substrate at room temperature. During the deposition procedure, the film received the thermal energy from the evaporation source and therefore the temperature of the film sandwiched with Rh or B was raising up to about 70°C. In the other cases, the temperature would be lower than 70°C. An electron beam gun was used as a heating device for the source materials, and a quartz oscillator as a thickness monitor. Whether the Fe film is stable or not, the thickness written in each figure means the average thickness of Fe film in preparation. In other words, the thickness is corresponding to the quantity of evaporated Fe atoms. The multilayer samples are listed in Table I. Fe source was enriched to 50% in Fe⁵⁷. The mylar sheet was 10cm square and apart by 25cm from the evaporation source. The vacuum during deposition was better than 1×10^{-7} torr. The alternate deposition process was repeated for several times to gain enough thickness for the Mössbauer measurements. The film was folded to be 2cm square in shape.

RESULTS AND DISCUSSION

Our experimental results are classified into two cases. First, Fe films as-deposited have already reacted with the covering materials or diffused into each other to make some compounds or alloys, that are, B-, Sn-, Rh-coated Fe films. Second, Fe films as-

Table II. Temperatures for Thermal Evaporation*

| material | melting point(°C) | T _{ev} ^{**} (°C) | atomic radius(Å) |
|------------------|-------------------|------------------------------------|------------------|
| Sb | 630 | 530 | 1.41 |
| Sn | 232 | 1250 | 1.41 |
| Fe | 1535 | 1480 | 1.16 |
| Rh | 1970 | 2040 | 1.25 |
| B | 2200 | 2000 | 0.80 |
| MgF ₂ | 1263 | 1130 | — |

* Reference 8.

** temperature for the vapor pressure of the material to become 10^{-2} torr.

deposited are stable, but the compound formation or the grain growth of Fe film happened by thermal treatments. The former is corresponding to the case of Sb-coated Fe film, and the latter to that of MgF_2 -coated Fe film. The melting point, the temperature for thermal evaporation, T_{ev} , and the atomic radius are listed in Table II.

I. Fe-Rh system

Figure 1 shows the Mössbauer spectra at 300K of Rh-coated Fe films. The fraction of the superparamagnetic single peak and that with smaller hyperfine field than that of bcc Fe are increasing with decreasing of the Fe film thickness. The single peak of the 16Å and 24Å Fe films completely disappeared at 4.2K. The 8Å Fe film shows only single line at 300K. The spectra at 4.2K of an 8Å film are shown in Fig. 2. Figures 2 (c) and (b) are the spectra of as-deposited Fe film coated with Rh with and without the external field of 45kOe respectively, and (a) is that of the same film left ten days at room temperature after the preparation. The spectrum (c) means that the fraction of six lines observed in (b) is in the ferromagnetic state and that the paramagnetic peak is corresponding to the inherent nonmagnetic material. From these two spectra, it is considered that the 8Å Fe film as-deposited has two different phases. One of them with six lines is attributed to ferromagnetic disordered α -phase of Fe-Rh alloys. The central peak may arise from nonmagnetic γ -phase. The Fe concentration ranges from 50 to 100 at.% for the disordered α -phase and from 0 to 30 at.% in Rh matrix for the nonmagnetic γ -phase according to Shirane *et al.*⁴⁾ The single line of 8Å Fe film at 300K is

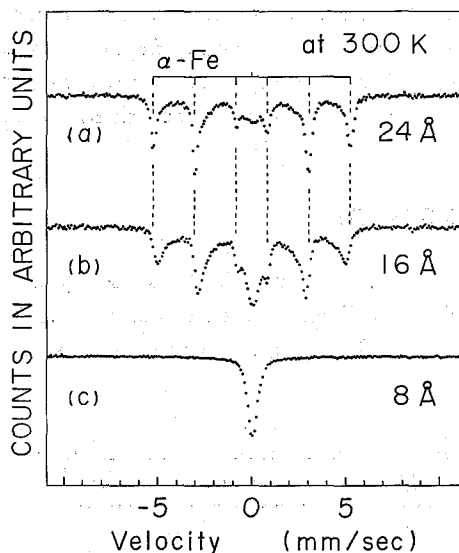


Fig. 1. The thickness dependence of Mössbauer spectra at 300K of the Rh-coated Fe films.

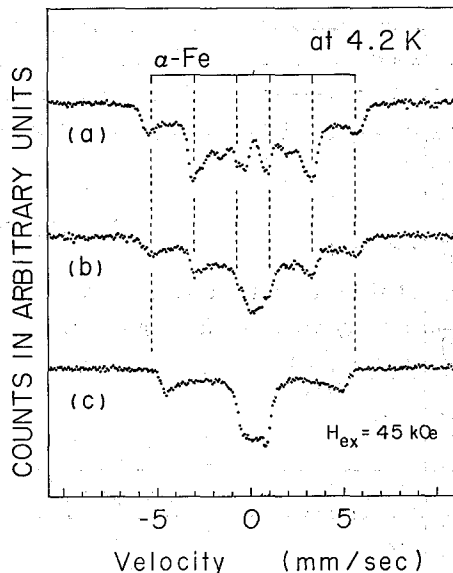


Fig. 2. The Mössbauer spectra at 4.2K of the 8Å Fe film coated by Rh layer. (a) the spectrum of the sample left ten days at room temperature after the preparation; (b), (c) the spectrum of the film as-deposited without and with the external field of 45 kOe, respectively.

constituted of the superparamagnetic behavior of ferromagnetic phase and the nonmagnetic γ -phase. When the 8Å Fe film was left ten days at room temperature after the preparation, nonmagnetic single peak disappeared and new lines were observed in the spectrum at 4.2K, Fig. 2(a). Comparing (a) with (b) in Fig. 2, the line shape of ferromagnetic components was not so different between (a) and (b) though the nonmagnetic single peak disappeared in (a). But the antiferromagnetic α -phase obviously shown in (a). It seems that Fe atoms in nonmagnetic γ -phase coalesced in some degree and form the antiferromagnetic α -phase. According to the phase diagram of this system, the coalescence of Fe impurities in γ -phase is hard to explain. We have not yet a conclusion about the explanation of this curious change from nonmagnetic to antiferromagnetic which occurs easily at room temperature. When Fe atoms were evaporated on a Rh layer, Fe-rich phases in the Fe-Rh alloys and α -Fe would be formed. Next, Rh atoms were deposited on the Fe layer and would diffuse to make Rh-rich phases. The content of Rh-rich or Fe-rich phases and α -Fe are depending on the Fe film thickness because the depth of interdiffusion is limited under the condition of sample preparation.

II. Fe-B system

Figures 3 and 4 show the Mössbauer spectra of Fe films sandwiched with B films at 300K and 77K, respectively. The 32Å and 24Å films have probably four components, those are α -Fe, Fe_2B (a), FeB (b), and Fe in B matrix(c). The amounts of components corresponding to (b) and (c) are increasing with decreasing of Fe thickness. In the

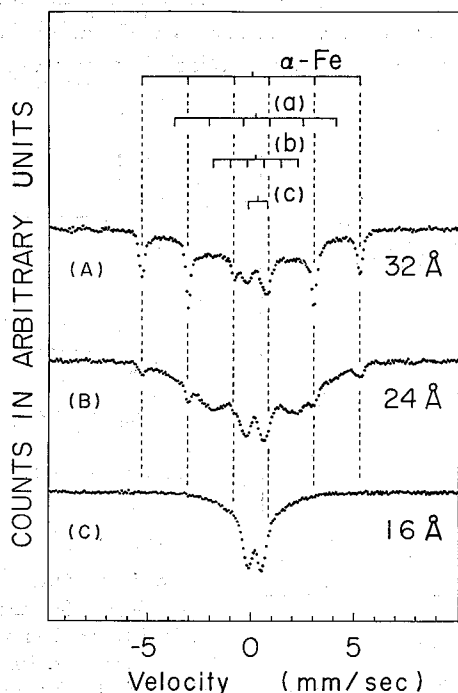


Fig. 3. The thickness dependence of Mössbauer spectra at 300K of the B-coated Fe films.

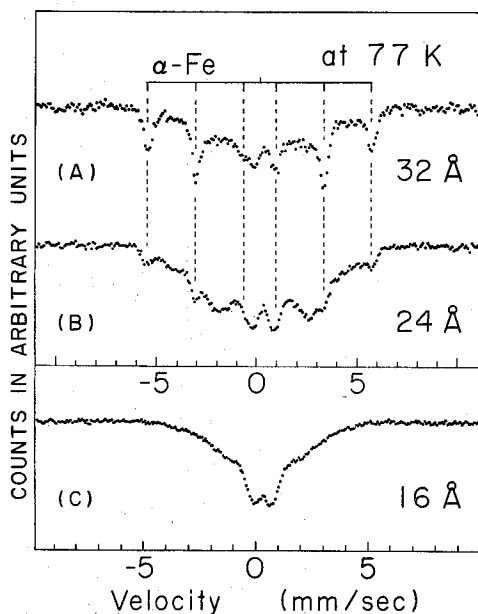


Fig. 4. The thickness dependence of Mössbauer spectra at 77K of the B-coated Fe films.

case of 16Å Fe film, all of Fe atoms form compounds with B whose concentration ranges from FeB to impurity Fe in B. The quadrupole doublet in 16Å Fe film does not disappear down to 4.2K, which is ascribed to no d-spin polarization state of Fe⁵⁷ atom. The quadrupole splitting is 0.64 mm/sec, and the isomer shift 0.23 mm/sec at 300K. These values are in agreement with Fe(1 at.%)B reported by Wäeppling *et al.*⁵⁾ In the 24Å Fe film, most of Fe atoms make compounds which are mainly consisted of FeB and the impurity Fe in B matrix. The diffusion after the preparation is not fast because the spectrum of each sample does not change for several months after. The compounds would be formed as follows. Evaporated Fe atoms would diffuse into B layer to make Fe-rich phase at the interface layer and evaporated B atoms also diffused into Fe substrate to make B-rich compounds. The main components of the compounds formed at the interface layer are B-rich compounds independent of the Fe film thickness. It means that B atoms diffused easily into Fe substrate because of their high kinetic energy and their small atomic radius.

III. Fe-Sn system

The sample was made by successive evaporation of Sn 400Å, Fe 48Å, and Sn 640Å in thickness in this order. The spectrum of as-deposited film at 300K has only a superparamagnetic single peak whose isomer shift is 0.49 mm/sec. The spectra at 4.2K are shown in Fig. 5. Figure 5(b) is corresponding to as-deposited film, and (a) is the spectrum after the thermal treatment for (b) at 200°C in vacuum about 14 hrs. The spectrum of as-deposited film shows a broad six lines and an α -Fe state does not exist, which means that the spectrum is constituted of some antiferromagnetic Fe-Sn compounds, that are, FeSn and FeSn₂.⁶⁾ After the thermal treatment, the spectrum is sharp six lines compared with (b) at 4.2K, and high temperature measurements of this sample are shown

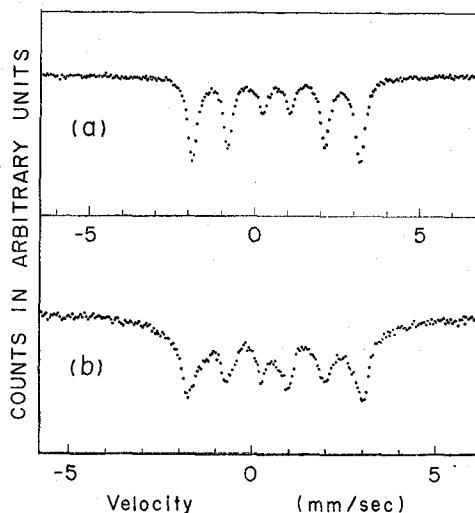


Fig. 5. The Mössbauer spectra at 4.2K of the Sn-coated Fe film.
(a) after the thermal treatment written in the text.
(b) as-deposited film.

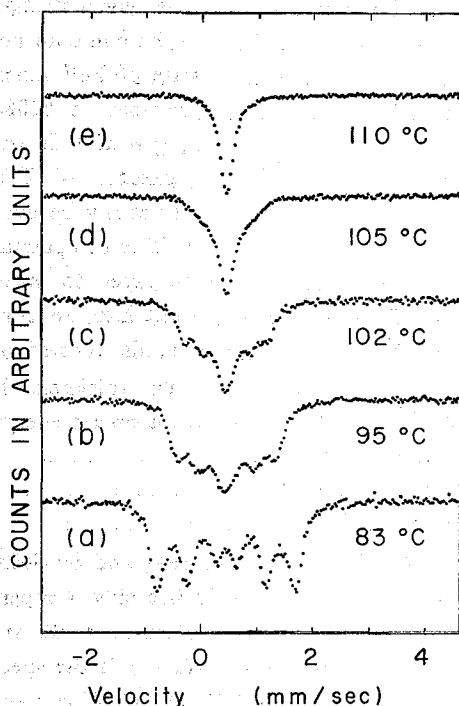


Fig. 6. The temperature dependence of the Sn-coated Fe film after the thermal treatment as described in the text.

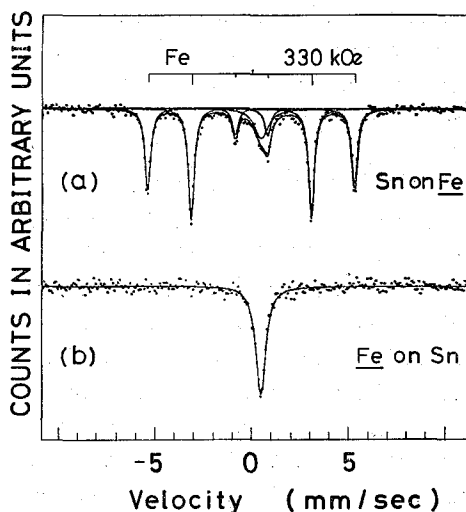


Fig. 7. The Mössbauer spectra at 300K.
(a) "Sn on Fe" sample,
(b) "Fe on Sn" sample. The solid lines show the computer fitting results.

in Fig. 6. During the thermal treatment, Fe and Sn atoms interdiffused each other and the grain growth took place. The grain growth results in the disappearance of superparamagnetic behavior at 300K. The Néel temperature of FeSn and FeSn₂ are 95°C and 107°C, respectively. The spectra at 95°C and 102°C are superposed with six lines of FeSn₂ and the paramagnetic single peak of FeSn. From the computer fitting results based upon the least squares method, the amount of FeSn₂ is 75% and the rest is FeSn. Comparing Fig. 5(b) with (a), the spectrum of as-grown film contained FeSn considerably. If Fe atoms diffused into a Sn matrix, FeSn was forming at the surface layer of a Sn substrate. In the reverse case, Sn-rich compounds like FeSn₂ would be made at the surface layer of an Fe substrate. It is most probable that Fe atoms are easily and successively diffused into a Sn layer. To make sure of this idea, "Sn on Fe" and "Fe on Sn" samples were prepared. The "Sn on Fe" sample is a 480Å Sn film evaporated on a 48Å Fe film at room temperature, and the "Fe on Sn" is a 48Å Fe on a 480Å Sn film. Figure 7 shows the Fe⁵⁷ Mössbauer spectra at 300K of these samples. Fe atoms of "Sn on Fe" mostly consisted of the metallic α -Fe state. The amount of superparamagnetic peak is nearly 15%, and the peak position is 0.50 mm/sec. The superparamagnetic single peak of Fig. 7(b) has an isomer shift of 0.49 mm/sec. The spectrum of "Fe on Sn" at 4.2K is similar to Fig. 5(b), and there is no peak resulting from α -Fe. These spectra mean that Fe atoms easily and successively diffuse into Sn matrix but Sn atoms are not easily diffusing into Fe. In the case of "Sn on Fe" film, deposited Sn

atoms make some compounds with Fe at first, but the further diffusion of Sn atom into Fe layer might be obstructed by the compounds because of its larger atomic radius and/or the deficiency of its kinetic energy enough to enhance the diffusion of Sn atom. In the case of "Fe on Sn" film, all of Fe atom diffused into Sn layer to make intermetallic compounds, perhaps mainly FeSn. It may be ascribed to both the high kinetic energy of evaporating Fe atom and the low melting point of Sn substrate.

IV. Fe-Sb system

Figure 8 shows the Mössbauer spectra of the Fe^{57} surface enriched Fe(111) film coated with Sb(0001) at elevated temperatures from 4.2K. The procedure of Fe^{57} surface enrichment is successive evaporations of Fe^{56} 120Å in thickness at first and next Fe^{57} 4Å on the evaporated Sb(0001) substrate at room temperature. The process was repeated for ten times as shown in Table I. Fe^{56} atom is inactive for the Mössbauer effect. The spectra in Fig. 8 are resulting from the surface layer of Fe film. Concerning both the structure and the magnetism of Sb-coated Fe film, we reported in other papers.^{3,7)} Up to 370K, α -Fe state is only observed, and paramagnetic doublet peak is a little recognized with α -Fe at 410K. Fe and Sb atoms are completely mixed to be in FeSb_2 state at 490K. The spectra of this surface enriched sample as-deposited are very similar to those of Sb-coated 8Å Fe thin film reported in Ref. 3. From both the surface enriched experiment and the thin film experiments, not only evaporated Fe atoms do not diffuse into Sb layer, but also evaporated Sb atoms do not into Fe layer at room temperature. The total amount of Sb atoms is much more than that of Fe atoms. From this quantitative difference, Fe and Sb interdiffused easily above 400K to make FeSb_2 .

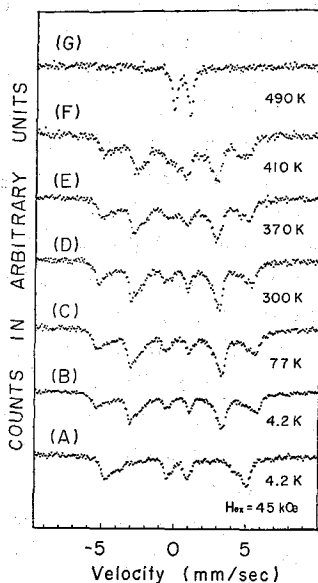


Fig. 8. The Mössbauer spectra of the Fe^{57} surface enriched Fe film coated by Sb layer at various temperatures. (A) under the external field of 45 kOe, (B)~(G) without the external field.

V. Fe-MgF₂ system

The spectra of (A), (B), and (C) in Fig. 9 are those of as-deposited 16Å Fe film sandwiched with MgF₂. (D), (E), and (F) are the spectra of the same sample after the thermal treatment at 480K in vacuum for twenty days. Neither the oxidation nor the compound formation was recognized in the spectra after the thermal treatment, but the fraction corresponding to the bulk α -Fe was more than the spectra before annealing. It is reported in the previous paper¹⁾ that the spectra of (A) and (B) in Fig. 9 are fully in the metallic and ferromagnetic state, and the fraction with larger hyperfine field than the bulk α -Fe is resulting from the surface layers of α -Fe coated with MgF₂. At 450K, the spectrum consisted of a superparamagnetic single peak resulting from the limited dimension of the Fe film. After the thermal treatment, the spectrum (D) at 480K shows the magnetic hyperfine pattern and the superparamagnetic single peak. Comparing the spectra at the same temperature before and after the thermal treatment, the difference is relative amounts of the bulk α -Fe, which is ascribed to the grain growth of the Fe film. This is the evidence that the fraction with larger hyperfine field than the bulk bcc Fe is attributed to the surface atoms.

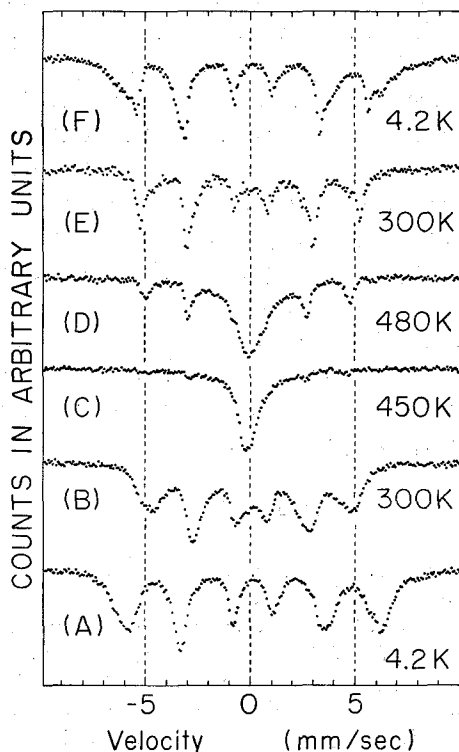


Fig. 9. The Mössbauer spectra of the 16Å Fe film at various temperatures. (A)~(C) as-deposited film, (D)~(F) after the thermal treatment as described in the text.

The kinetic energy of evaporated atom is estimated from the evaporation temperature, T_{ev} . Whether the sandwiched Fe film is stable or forms some compounds with substrate material would depend upon the followings; (i) the melting point of the sub-

strate material, (ii) the kinetic energy of evaporating atoms, and (iii) the chemical affinity between the deposited atom and the substrate. Whether a thin film is continuous or has an island structure, the aggregation of evaporated atoms has a much larger surface area than the bulk. The high surface energy would make the thin film active. The threshold value of the compound formation energy in the multilayer thin film would be lower than that in the bulk case. The depth of diffusion would be determined by the kinetic energy of evaporated atom and the melting point of the substrate material. As the kinetic energy of evaporated atom is higher and the melting point of the substrate material is lower, the evaporated atom diffuses more easily and deeper into the substrate.

Consider such a case that a high T_{ev} material evaporated on a substrate of low melting point. Evaporated atoms would give some energy to make the substrate atoms mobile. Then, evaporated atoms are easily diffused into the substrate. Fe-Sn system is corresponding to this case. The spectra of a "Sn on Fe" film and an "Fe on Sn" sample in Fig. 9 mean that Fe atoms easily and successively diffused into Sn matrix, but Sn atoms were not easily diffusing into Fe. It may be ascribed to both the high kinetic energy of evaporating Fe atom and the low melting point of Sn substrate. On the other hand, the compound formation or diffusion did not take place in the Fe-Sb system, though Sb has a relatively low melting point. As Sb is easily sublimated, that is, the kinetic energy is low, it would be easily understood that Sb atom could not diffuse into Fe layer. The kinetic energy of evaporated Fe atom may not be sufficient for the diffusion into Sb matrix or the compound formation. When each component of multilayer film has a high melting point and also a high evaporation temperature, compounds were also formed such as the Fe-Rh and the Fe-B system. In these cases, it is assumed that the kinetic energy of either or both components overcomes the threshold value of the formation energy of any compound. Especially in Fe-B system, the small atomic radius of B atom is one of the important factors in the diffusion. From these considerations, the important factor determining the compound formation is the kinetic energy of evaporated atom, that is, the evaporation temperature. The melting point of substrate material would be concerned whether the successive diffusion of evaporated atom is allowed or not during the sample preparation.

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